

Assessing phosphorus bioavailability in agricultural soils and runoff

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Abstract

Bioavailable phosphorus (BAP) transported in agricultural runoff can accelerate surface water eutrophication. Although several algal assays and chemical extractions have been proposed to estimate BAP, procedural and theoretical limitations have restricted widespread BAP measurement. Thus, a routine method was developed to estimate BAP, which uses iron oxide-impregnated paper strips (Fe-oxide strips) as a P-sink for BAP in runoff. In the proposed method BAP is determined by shaking 50 mL of unfiltered runoff with one Fe-oxide strip for 16 h. Phosphorus is removed from the strip by 0.1 M H_2SO_4 and measured. The BAP content of runoff from 20 agricultural watersheds in the Southern Plains was related to the growth of P-starved algae incubated for 29 d with runoff as the sole source of P. Acting as a P sink, Fe-oxide strips may have a stronger theoretical basis than chemical extraction in estimating BAP. The method may also have potential use as an environmental soil P test to indicate soils liable to enrich runoff with sufficient P to accelerate eutrophication. Bioavailable P loss in runoff was lower from no till ($438 \text{ g ha}^{-1} \text{ yr}^{-1}$) than from conventional till ($1288 \text{ g ha}^{-1} \text{ yr}^{-1}$). Kinetic and enrichment ratio approaches accurately predicted (r^2 of 0.93) BAP transport in runoff during 1988 to 1990. Use of the Fe-oxide strip method will facilitate estimation of BAP transport in runoff and thereby, improve assessment of the resultant impact on the biological productivity of receiving surface waters.

Abbreviations: A: Degree of soil aggregation (unitless); B: Soil bulk density (Mg m^{-3}); BAP: Bioavailable P content of runoff (mg L^{-1} and kg ha^{-1}); BIOP: Bioavailable P content of soil (mg kg^{-1}); BPP: Bioavailable particulate P content of runoff (mg L^{-1} and kg ha^{-1}); D: Effective depth of interaction between runoff and surface soil (mm); DP: Dissolved P content of runoff (mg L^{-1} and kg ha^{-1}); ER: Enrichment ratio (unitless); P: Phosphorus; P_a : Bray I available P content of 0–50 mm depth of soil (mg kg^{-1}); PP: Particulate P content of runoff (mg L^{-1} and kg ha^{-1}); STP: Soil test P, plant available (mg kg^{-1}); TP: Total P content of runoff (mg L^{-1} and kg ha^{-1}); t: Duration of runoff event (min); W: Runoff water/soil (suspended sediment) ratio (L g^{-1}); K, α , β , i: Constants of the equation describing the kinetics of soil P desorption.

Introduction

Bioavailable phosphorus (BAP) transported in agricultural runoff can accelerate surface water eutrophication [7, 8]. Bioavailable P represents

orthophosphate that is potentially available for algal uptake and comprises P in dissolved (DP) and particulate (PP) forms. Dissolved P is mostly available for algal uptake [25]. However, PP, which encompasses P associated with sediment

and organic material eroded during runoff, contributes a variable but long-term source of potentially bioavailable PP (BPP) to lakes. Sharpley *et al.* [38] observed that the BAP content of runoff, estimated by 0.1 M NaOH extraction, increased from 20 to 80% of total P (TP) transported in runoff with less tillage and increasing residue cover. The varying amounts and bioavailabilities of DP and PP transported in different runoff events, stress the need for accurate measurements of BAP to evaluate the impact of agricultural runoff on accelerated eutrophication.

Bioavailable P measurement by 7 to 100 d algal assays [18] does not lend itself to routine analysis. Thus, more rapid chemical extractions, using NH_4F , NaOH, and anion exchange resins, have been used to simulate removal of DP and BPP by algae [5, 34]. However, the amount of P extracted depends on the ionic strength, cationic species, and pH of the extractant, and solution:soil ratio used [6, 35]. Also the validity of relating the form or availability of P in a chemical extractant to P bioavailability in the aquatic environment is questionable.

A simpler method is proposed. The principle of the method uses a strip of iron oxide-impregnated filter paper (Fe-oxide strip) as a P-sink to adsorb BAP from a sample of runoff or sediment, and subsequent removal of P by dilute acid [32]. The method is developed from Menon *et al.* [15, 17], who successfully used Fe-oxide strips to estimate plant available P in a wide range of soils and management systems [16, 31]. Sharpley [32] observed that the Fe-oxide strip P content of runoff sediment was closely related ($r^2 = 0.96$) to the growth of P-starved *Selenastrum capricornutum* incubated for 29 d with runoff as the sole source of P.

There has been an increase over the last decade in the percentage of agricultural soils testing high or excessive for P in areas of intensive livestock and crop production [40]. This has stimulated interest in using soil testing to identify and monitor with time, the potential for excessive P enrichment of surface waters by soils. Thus, there is a need for environmental soils tests that assess the forms of soil P important to eutrophication rather than plant availability. Wolf *et al.* [44] reported that soil BAP (0.1 M NaOH extractable P) was related to soil

test P (STP) determined by Bray, Mehlich, and Olsen methods for 91 noncalcareous soils. However, the relationships between soil BAP and STP varied with oxalate extractable Fe and Al content of the soils. Clearly, STP methods developed to assess plant available soil P should not be adopted as environment soil tests to assess the potential of a soil to enrich the P content of runoff. It is possible that the Fe-oxide strips may have potential use as an environmental soil P test to estimate the BAP content of soil or runoff.

This paper summarizes the development of a Fe-oxide strip method to estimate the BAP content of agricultural soils and runoff. The effect of management on BAP transport in runoff from 8 grassed and 12 cropped watersheds in the Southern Plains over a 3-year period, is investigated using the Fe-oxide strips. Finally, BAP transport in runoff is predicted using soil BAP and kinetic and enrichment ratio equations, and compared with measured values.

Materials and Methods

Soil collection and analysis

Surface samples (A1 or Ap horizons) and supporting laboratory and taxonomic data for 203 soils, representing all soil orders from the continental U.S., Puerto Rico, Indonesia, Malaysia, Papua New Guinea, Philippines, and Sudan were obtained from the Soil Management Support Service, Soil Conservation Service (SCS), National Soil Survey Laboratory, Lincoln, Nebraska. All soils were air-dried and sieved (2 mm).

Clay content of the soils was determined by pipet analysis following dispersion with sodium hexametaphosphate [3]. Cation exchange capacity (CEC) was determined by direct distillation of adsorbed NH_4 following leaching of 25 g soil with 250 mL of 1.0 M NH_4OAc (pH 7.0) [41]; organic C by the dichromate-wet combustion procedure [26]; calcium carbonate (CaCO_3) equivalent by treatment with dilute acid and titration [1]; and soil pH using a glass electrode at a 5:1 water:soil ratio (wt/wt). Extractable Fe and Al was determined by allowing 4 g of soil to stand in 40 mL of 1 M NH_4OAc (adjusted to pH

4.8) for 2 h. Iron and Al concentrations of filtered extracts were measured by the colorimetric orthophenanthroline [22] and aluminon [12] methods, respectively.

Soil test P was measured by Bray I, Mehlich III, and Olsen procedures. Bray I P was extracted by shaking 2 g soil with 20 mL of 0.03 M NH_4F and 0.025 M HCl for 5 min [2]. Mehlich III P was extracted by shaking 2 g soil with 20 mL 0.2 M CH_3COOH , 0.25 M NH_4NO_3 , 0.015 M NH_4F , 0.013 M HNO_3 , and 0.001 M EDTA for 5 min [13]. Olsen P was extracted by shaking 1 g soil with 20 mL of 0.05 M NaHCO_3 (pH 8.5) for 30 min [21]. The strip P content of each soil sample was determined by shaking a 1 g soil sample in 40 mL 0.01 M CaCl_2 and Fe-oxide strip end-over-end for 16 h at 25 °C. Iron-oxide strip preparation and methodology is described later. Total P (TP) content was determined by perchloric acid digestion [20].

The strip is then removed, rinsed free of adhering soil particles, and dried. Phosphorus retained on the strip was removed by shaking the

strip end-over-end with 40 mL 0.1 M H_2SO_4 for 1 h and measured. Resin P was determined on soil ground to pass a 0.15 mm sieve by end-over-end shaking of 5 cm³ IRA-400 anion exchange resin (0.25 to 1.18 mm, bicarbonate form) with 4 g soil in 40 mL water for 16 h. A 0.15 mm screen was used to separate resin from soil. Phosphorus was removed from the resin with 100 mL 1.5 M NaCl for 24 h with occasional stirring. In all extracts, P concentration was measured on neutralized filtrates by the colorimetric method of Murphy and Riley [19].

Watersheds

Management characteristics of the 20 watersheds are summarized in Table 1 and represent agricultural land use in the Southern Plains region of Oklahoma and Texas. Reduced tillage of dryland wheat (*Triticum aestivum* L.) – sorghum (*Sorghum bicolor* (L.) Moench.) – fallow rotation at Bushland consisted of stubble mulch tillage, with sweeps used to kill weeds. Conventional tillage of wheat at El Reno consisted of ploughing

Table 1. Watersheds characteristics for 1988 to 1990

Watershed	Management	Soil type	Annual rainfall (cm)	Fertilizer P applied (kg ha ⁻¹ yr ⁻¹)
<i>Bushland, Texas</i>				
B10A } B11A } B12A }	No till wheat-sorghum-fallow rotation	Pullman clay loam (Torretic)	54	0
B10B } B11B } B12B }	Reduced till wheat-sorghum-fallow rotation	Paleustolls		0
<i>El Reno, Oklahoma</i>				
E1	Native grass	Kirkland silt loam	75	0
E2	Native grass	loam		2
E3	Native grass	(Udertic)		0
E4	Native grass	Paleustolls		2
E5	Wheat-sorghum rotation			16
E6	Conventional till wheat			12
E7	No till wheat			13
E8	Conventional till wheat			13
<i>Ft. Cobb, Oklahoma</i>				
C1 } C2 }	Peanuts-grain sorghum rotation	Cobb fine sandy loam (Udic Haplustalfs)	90	19
				18
<i>Woodward, Oklahoma</i>				
W1	Native grass	Woodward loam	60	0
W2	Native grass	(Typic)		0
W3	Native grass	Ustochrepts)		23
W4	Native grass			23

(chisel, E5; moldboard, E6; and sweeps, E8). At Ft. Cobb, conventional tillage of the peanut (*Arachis hypogaea* L.)–sorghum rotation consisted of ploughing (chisel and/or moldboard) followed by harrowing and disking before planting. Weed control on the no till wheat watersheds at El Reno was primarily with phenoxy and glyphosate herbicides. Fertilizer P was applied at the fall planting of wheat at El Reno and during harrowing in March at Ft. Cobb at rates determined by soil test recommendations.

Watershed runoff was measured using pre-calibrated flumes equipped with water-level recorders, with 5 to 15 samples collected automatically during each runoff event. The samples were composited in proportion to flow, to provide a single representative sample, stored at 4 °C until analysis.

Aliquots of runoff samples were centrifuged [$266 \times 10^5 \text{ cm sec}^{-1}$ ($15000 \times g$) for 5 min] and filtered ($0.45 \mu\text{m}$) prior to DP determination by the colorimetric method of Murphy and Riley [19]. The same method was used for TP, following perchloric acid digestion of unfiltered samples and neutralization of the digest [20]. Particulate P was calculated as the difference between TP and DP. Suspended sediment concentration of runoff was determined in duplicate as the difference in weight of 250 mL aliquots of unfiltered and filtered runoff after evaporation (105°C) to dryness.

Algal assay

Suspended sediment in runoff from 9 watersheds (E5, E6, E7, E8, C1, C2, W2, W3, and W4) was collected for use as the P source in algal assays. Samples from four runoff events in May and June, 1986 were combined as were three events in May and June, 1987 and sediment concentrated by centrifugation and decantation. The sediment concentration of each slurry was sterilized by autoclaving at 121°C and 104 Pa before P analysis and algal assay inoculation.

The BAP content of each sediment sample was determined by Fe-oxide strip methodology described below. The total P (TP) content of each sediment sample was determined by digestion with perchloric acid [20]. The concentration of P was measured on neutralized filtrates of all extracts by the colorimetric method of Murphy

and Riley [19]. Preliminary studies indicated that autoclaving did not affect the amount of P extracted by the above methods, suggesting similar availability of P to algae before and after sterilization.

Anabaena, *Ankistrodesmus*, *Euglena*, and *Selenastrum* were cultured in Provisional Algal Assay Procedure medium [23], with fluorescent and incandescent light at an intensity of 90 W m^{-2} . At the stationary growth phase, algal cells were rinsed in P-free PAAP medium and incubated in light at 22°C until the culture began to yellow (approximately 15 d), indicating the onset of P deficiency in cells. Cells were incubated for an additional 5 d before incubation with runoff sediment.

An aliquot (2 mL) of the sediment slurry (approximately 0.1 g sediment) was added to 57 mL of P-free PAAP medium in 250 mL Erlenmeyer flasks. The suspension was inoculated with the P-staved algae to attain cell densities of $5 \times 10^4 \text{ cells mL}^{-1}$ for a 29-d incubation period at a light intensity of 90 W m^{-2} at 22°C . Duplicate flasks were prepared and shaken twice daily. After incubation, three subsamples were removed from each flask and 8 replicate cell counts were made with an improved Neubauer hemacytometer.

Preparation of Fe-oxide strips

Filter-paper circles (15-cm diameter, Whatman No. 541¹) were immersed in a 10% (w/v) solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. The paper circles were then air dried and immersed in 2.7 M NH_4OH solution to convert FeCl_3 to Fe oxide. Immersion in NH_4OH was carried out as rapidly as possible to avoid uneven oxide deposition on the paper [11]. After the paper circles were air-dried, they were cut into strips 10 by 2 cm and stored for later use.

Proposed Fe-oxide strip method

One Fe-oxide strip is shaken with 50 mL of unfiltered or filtered runoff for 16 h on an end-over-end shaker at 25°C . The strip is then removed, rinsed free of adhering soil particles, and dried. Phosphorus retained on the strip is removed by shaking the strip end-over-end with

¹ Mention of trade names implies no endorsement by USDA.

40 mL of 0.1 M H_2SO_4 for 1 h, and following neutralization is measured by the method of Murphy and Riley [19]. For unfiltered runoff, P retained on the strip represents that associated with both dissolved and particulate forms. For filtered runoff, P retained on the strip represents dissolved orthophosphate.

Results and discussion

Development of the Fe-oxide strip method

In developing the Fe-oxide strip method the effect of contact time between strip and sample, recovery of added P by the strips, reproducibility of recovery, algal availability and storage time were investigated.

Contact time

The effect of contact time on the extraction of P from runoff sediment was determined by shaking Fe-oxide strips with sediment (1 g in 50 mL of water, a sediment concentration 20 g L^{-1}). Removal of P by the strips was essentially complete after 8 h [32]. However, an extraction time of 16 h (i.e., overnight) is recommended for analytical convenience and subsequent strip P data are for a 16 h extraction.

A similar pattern of P removal with time by strips was obtained at sediment concentrations ranging from 1 to 40 g L^{-1} . These concentrations are within the range observed for individual runoff events from the 20 watersheds during 1988 to 1990 (0.1 to 31.41 g L^{-1}).

P recovery

The recovery of P by Fe-oxide strips exceeds 90% of P added (as K_2HPO_4) in standard solutions containing up to 3.0 mg P L^{-1} (Table 2). The range in P covers DP concentrations found in runoff from the 20 watersheds during 1988 to 1990 (0.01 to 2.32 mg L^{-1}). In spite of the slight decrease in percent P recovery with increasing P concentration, there was a significant ($p < 0.001$) positive relationship ($y = 0.91x + 0.004$, $r^2 = 0.99$) between the concentration of P removed by the strips and that added (Table 2). A similar relationship ($y = 0.91x + 0.005$, $r^2 = 0.99$) between strip P recovery and P

Table 2. Concentration and percent recovery of P by Fe-oxide strips

Dissolved P concentration	Strip P	Percent recovery
-----(mg L^{-1})-----		(%)
0.01	0.010	100
0.05	0.047	94
0.10	0.093	93
0.25	0.233	93
0.50	0.460	92
0.75	0.690	92
1.00	0.911	91
2.00	1.823	91
3.00	2.701	90

added in P concentrations up to 0.05 mg L^{-1} was found by Menon [14].

Strip reproducibility

The reproducibility of P removal by Fe-oxide strips was evaluated within and between separately prepared batches of strips. For Fe-oxide strips produced in the same batch, little variation was found in the amount of P removed by 10 different strips from sediment slurries collected from watersheds E6 and W2 (Table 3). Similar amounts of P were also removed from E6 and W2 slurries by strips from separately prepared batches (Table 3). The standard deviation for both within and between batches was less than 3% of the mean, which indicates that the Fe-oxide strips can provide a highly reproducible estimate of BAP.

Algal availability

The FE-oxide strip P content of runoff sediment was linearly related ($p < 0.001$) to the growth of P-starved algae, incubated for 29 d with runoff sediment as the sole source of P (Fig. 1). Similar relationships were also observed for 2 and 15 d incubations using *Selenastrum* only [32]. Thus, strip P provides an estimate of the bioavailable P (BAP) content of runoff that may be potentially available for uptake by these freshwater algae common in the Southern Plains [43]. Caution must be exercised, however, in relating BAP estimates by the Fe-oxide strip or any other incubation method, that estimate P bioavailability under optimum conditions to a quantitative *in situ* value of BAP in lakes.

Table 3. Phosphorus removed by 10 Fe-oxide strips of the same and different production batches from watershed runoff sediment

	Strip phosphorus (mg kg ⁻¹)			
	Same production batch		Different production batch	
	E6	W2	E6	W2
	102	253	101	257
	98	250	97	257
	101	256	100	255
	102	248	103	250
	100	251	102	248
	104	250	100	250
	102	254	98	256
	97	252	104	257
	99	248	102	249
	100	250	98	247
Mean	101	251	101	253
Standard deviation	±2.0	±2.4	±2.2	±3.9

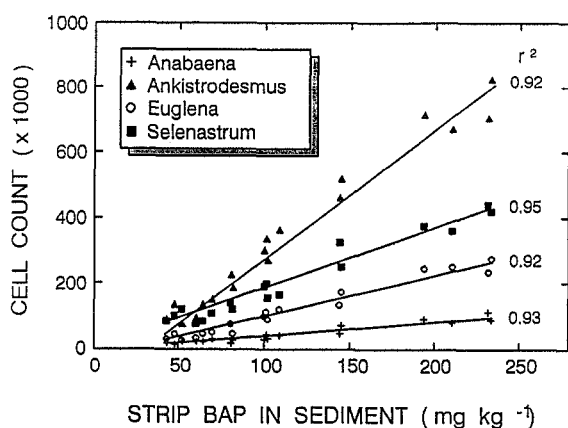


Fig. 1. Relationship between the strip bioavailable P content of runoff sediment and growth of P-starved algae during a 29-day incubation.

Storage time

The effect of storage time between the extraction of runoff with Fe-oxide strips and P analysis was evaluated using runoff sediment from watersheds E6 and W2. The amount of P removed from runoff sediment by strips was not significantly ($p < 0.001$) affected by the length of time between strip extraction of the runoff sample and acid extraction of the strip (Table 4). Thus, prepared strips may be sent to a given location for BAP extraction, dried, and returned to an analytical laboratory for P removal and measurement up to 2 months later.

As a more realistic test, Fe-oxide strips prepared in the USA, were sent to laboratories in Bologna and Rome, Italy for BAP determination

Table 4. Phosphorus removed from runoff sediment by Fe-oxide strips as a function of time between sediment and acid extraction

Time between sediment and acid extraction	Runoff sediment	
	E6	W2
days	(mg kg ⁻¹)	
0	98	252
1	97	253
3	102	248
6	99	251
10	104	254
17	102	254
24	96	252
31	99	247
60	103	250

on simulated and actual runoff water. Following overnight shaking of Fe-oxide strips with runoff samples, P was removed from the strips and analyzed in either Bologna or Rome and on duplicate strips returned to the USA. Amounts of Fe-oxide strip P in runoff determined in either Bologna or Rome were not significantly different ($p < 0.001$) from values measured in the USA (Fig. 2). Slope and intercept values of the relationship between Italian and USA determined Fe-oxide strip P, were almost 1 and 0, respectively.

The close agreement between the concentration of Fe-oxide strip P in runoff measured in both Italian and USA laboratories, indicates that the simplicity of the proposed method can give highly reproducible BAP estimates. This was the case even though different personnel extracted P

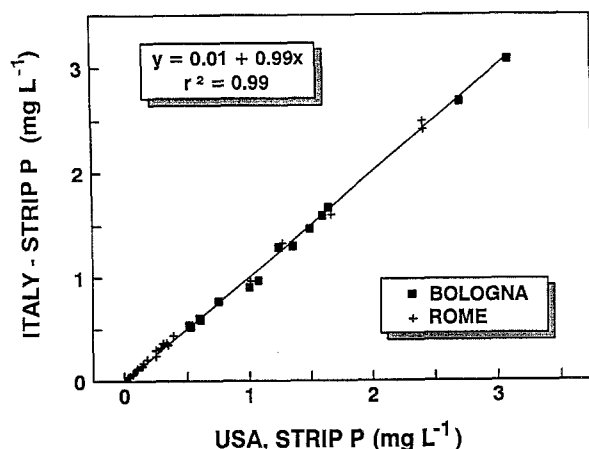


Fig. 2. Relationship between the Fe-oxide strip P concentration of runoff extracted in Italy and duplicate strips analyzed in Italy and the USA.

from the strips and conducted the colorimetric analysis at each laboratory. Thus, prepared Fe-oxide strips may be sent to another location and BAP measured using only a 100 to 500 mL bottle in which a strip and runoff sample are shaken overnight. The Fe-oxide strip may then be air dried and returned to an analytical laboratory for P removal and measurement.

Bioavailable P content of soil

Soil groups

The 203 soils were divided into three groups, calcareous, slightly, and highly weathered, based on taxonomic and chemical characteristics out-

lined earlier by Sharpley *et al.* [36]: calcareous soils – soils with free calcium carbonate (56 soils in this group); *highly weathered soils* – Oxisols, Utisols, Quartzipsamments, Ultic subgroups of Alfisols, and acidic Ochrepts (67 soils in this group); and *slightly weathered soils* – all other soils (mostly Mollisols) (80 soils in this group). The above grouping does not represent an exact sequence of degree of weathering and some overlap may exist between groups. However, it is used as the soils in each group behaved similarly, in terms of relationships between P forms [36].

Differences in soil properties between the three groups are consistent with the effect of pedogenesis on soil physical and chemical processes. A general decrease in pH and increase in organic C and extractable Fe and Al content with an increase in the degree of soil weathering was apparent (Table 5). A lack of information on fertilizer P history of the Ap soil samples, prevents a comparison of P contents between groups. The wide range in soil properties affords a comparison of the amount and forms of P extracted by Fe-oxide strips and STP.

Soil test P relationships

Strip P was closely related to resin P for all soils (Fig. 3). For each group of soils this relationship was close to 1:1, with strip P – resin P regression slopes almost 1 (Table 6). Strip P was also closely related to P tests for soils on which the use of the test is recommended. For example,

Table 5. Physical and chemical properties of the soils used

Property	Calcareous (56)*		Slightly weathered (80)		Highly weathered (67)	
	Mean	Range	Mean	Range	Mean	Range
Clay, %	26	3–57	23	6–62	23	1–76
pH	7.9	7.0–9.1	6.5	5.1–8.3	5.0	3.9–6.8
Organic C, g kg ⁻¹	11	1–47	14	1–49	24	4–117
CEC, mmol kg ⁻¹	232	13–771	207	53–438	119	13–432
CaCO ₃ , g kg ⁻¹	55	5–540	–	–	–	–
Extractable Fe, mg kg ⁻¹	6.5	0.1–17.1	11.9	0.1–43.3	19.9	0.1–86.0
Extractable Al, mg kg ⁻¹	3.4	0.2–7.2	4.7	0.5–14.8	19.0	2.7–97.0
Resin P, mg kg ⁻¹	14	1–56	19	4–56	7	1–43
Strip P, mg kg ⁻¹	13	1–58	16	4–48	6	1–37
Bray I P, mg kg ⁻¹	16	1–80	25	4–93	33	3–206
Mehlich III P, mg kg ⁻¹	29	1–358	22	3–75	22	1–147
Olsen P, mg kg ⁻¹	12	1–62	14	1–42	12	1–50
Total P, mg kg ⁻¹	545	89–2006	475	77–1505	437	43–1429

* Number in parentheses is the number of soils in each group.

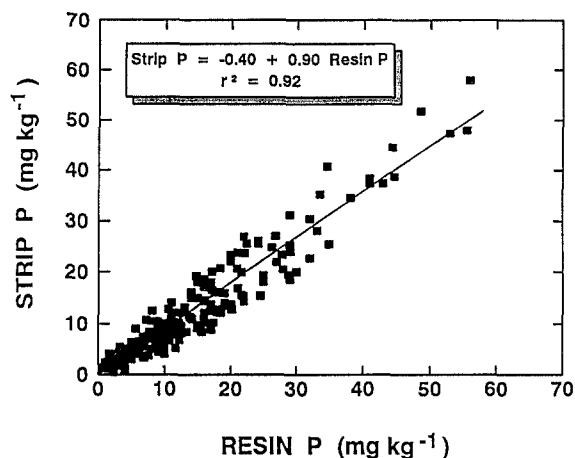


Fig. 3. Relationship between the amount of P extracted from 203 soils by Fe-oxide strips and anion exchange resin.

Olsen P in calcareous soils, and Bray I and Mehlich III P in slightly and highly weathered soils were most closely related to strip P.

Resin P is considered to represent more accurately plant available P across a wider range of soils than other methods (e.g., Bray I, Mehlich III, and Olsen) [4, 39]. Thus, strip P may extract amounts of P related to plant availability for a wide range of soils. However, different amounts of P were extracted by Fe-oxide strips and soil P tests for any given soil (Tables 5 and 6). For example, averaged for each group, Bray I extracted 1.8 times more P than Fe-oxide strips for slightly weathered soils and 5.8 times more for highly weathered soils (Table 6). For calcareous soils, average P recovery by the Olsen extractant was lower than by Fe-oxide strips. Thus, STP may not reliably represent the potential pool of bioavailable P in soil that can be released to runoff.

Because of the simplicity of the Fe-oxide strip method in determining bioavailable soil P, its measurement should not be substituted by STP

in efforts to evaluate the relative effects of agricultural management on potential BAP loss in runoff. This does not mean that Fe-oxide P should be determined on all soils analyzed by soil test laboratories. It is suggested STP be used as an initial indicator of soils liable to enrich runoff with sufficient P to accelerate eutrophication. Additional information could then be provided by the Fe-oxide strip method on soils identified as vulnerable to P loss.

Sampling protocol for tests to evaluate the environmental impact of soil P, may also need to be reevaluated. Most soil samples submitted to soil test laboratories are collected over a 0 to 20 cm depth. However, the depth of soil interacting with runoff water is generally less than the surface 2 cm of soil [29]. As P is relatively immobile in soils, the surface 2 cm of soil may be highly enriched in P, relative to the 0 to 20 cm depth. The accumulation will be of particular importance in soils under reduced or no till practices, where less soil mixing and P incorporation occurs than with conventional tillage.

Bioavailable P content of runoff

The mean annual loss of soil and P in runoff from 1988 to 1990 is summarized as a function of watershed management in Table 7. Bioavailable P was determined by Fe-oxide strips on unfiltered runoff samples. Soil and P loss was reduced by practices minimizing erosion and runoff, with BAP losses of 1228 and 177 g ha⁻¹ yr⁻¹ from conventional till and grassed watersheds, respectively (Table 7). The loss of BAP from no till wheat (E7, 1255 g ha⁻¹ yr⁻¹) was appreciably greater than from the other no till and reduced till watersheds (106 to 304 g ha⁻¹ yr⁻¹), which results in part from the application of fertilizer P to E7 only. However, the loss of

Table 6. Slope and coefficient of determination (r^2) for the regression between the soil content of strip P and other P forms

P form	Calcareous		Slightly weathered		Highly weathered	
	Slope	r^2	Slope	r^2	Slope	r^2
Resin	0.94	0.92***	1.01	0.90***	1.03	0.93***
Bray I	0.87	0.78***	1.75	0.90***	5.84	0.96***
Mehlich III	0.44	0.44**	1.39	0.89***	3.90	0.96***
Olsen	0.89	0.89***	0.52	0.58**	1.26	0.27*

*, **, and *** designate 5.0, 1.0 and 0.1% significance, respectively.

Table 7. Mean annual soil loss; runoff; and amount of dissolved P, bioavailable P, and total P in runoff for 1988 to 1990

Watershed	Soil loss	Runoff	Dissolved P	Bioavailable P	Total P
	kg ha ⁻¹ yr ⁻¹	mm	-----g ha ⁻¹ yr ⁻¹ -----		
<i>Native grass</i>					
E1	18	16.17	96	157	227
E2	23	14.38	131	226	262
E3	35	15.75	118	192	225
E4	16	15.01	361	435	468
W1	25	1.13	13	19	31
W2	77	0.58	9	15	54
W3	244	4.45	221	278	334
W4	104	1.84	68	96	100
Mean	68	8.66	127	177	213
<i>No till</i>					
B10A	230	2.70	86	161	295
B11A	398	4.34	70	181	439
B12A	707	3.98	82	156	352
E7	196	17.38	1087	1255	1461
Mean	383	7.10	31	438	637
<i>Reduced till</i>					
B10B	847	1.64	30	189	532
B11B	648	1.84	34	106	391
B12B	2684	6.52	84	304	1522
Mean	1393	3.33	49	200	815
<i>Conventional till</i>					
C1	12314	20.42	249	1631	5036
C2	23257	18.57	211	2355	9958
E5	92	12.99	1055	1253	1347
E6	5719	13.12	191	540	2364
E8	312	10.96	255	360	597
Mean	8339	15.21	392	1228	3860

BAP from no till wheat (1255 g ha⁻¹ yr⁻¹) was even greater than from conventionally tilled wheat (540 and 360 g ha⁻¹ yr⁻¹), although similar amounts of fertilizer P were applied to each watershed (12 to 13 kg P ha⁻¹ yr⁻¹) (Table 1 and 7). The elevated BAP losses from E5 may result from an increased vegetative soil cover afforded by the summer crop of sorghum, while E6 and E8 remained fallow.

A potentially greater loss of fertilizer P as BAP in runoff from no till (9% for E7) than conventionally tilled wheat (3 and 1% for E6 and

E8) was calculated, assuming native BAP losses of 177 g ha⁻¹ yr⁻¹ (Tables 1 and 7). This emphasizes the need for judicious fertilizer management particularly on no till practices. This should include subsurface placement of P to minimize surface accumulations.

Although P loss in runoff was lower from reduced and no till compared to conventional till watersheds, the proportion of P transported in bioavailable forms (DP and BPP) was greater for the former watersheds (Table 8). For example, BAP comprised a larger portion of TP loss from

Table 8. Percent bioavailability of total and particulate loss in runoff averaged for the different management practices

Management	Bioavailable P	Dissolved P	Bioavail. Partic. P
	Total P	Bioavailable P	Particulate P
	-----%		
Native grass	83	72	58
No till	69	76	35
Reduced till	25	25	20
Conventional till	32	32	24

no till (69%) compared to conventionally tilled wheat (32%). This may be attributed to an increasing contribution to BAP of DP (32% for conventional and 76% for no till) leached from plant material and BPP to PP (24% for conventional and 35% for no till) with preferential transport of clay-sized particles in runoff, accentuated by vegetative soil cover (Table 8).

A similar proportional increase in DP transport from no till watersheds with unincorporated residues compared to conventionally tilled watersheds with incorporated residues has been reported [9, 10, 24]. The increased transport of DP under no till was attributed to leaching of P from residue material. The increase in bioavailability of PP transported in runoff from watersheds with greater vegetative cover (Table 8), results from an increase in the proportion of clay-sized ($<2\ \mu\text{m}$) particles of higher P content rather than coarser ($>2\ \mu\text{m}$) particles transported as soil loss decreased [38]. Further, PP bioavailability may increase with a decrease in size of eroded soil particles, which contain larger amounts of more highly sorbed P and a decreasing proportion of primary mineral P (i.e., apatite) of lower availability compared to coarser silt-sized particles [37, 42].

Predicting Bioavailable P Loss in Runoff

Bioavailable P is comprised of DP and BPP, which have different origins and modes of transport. Dissolved PP originates from soil P extraction and dissolution during interaction with rainfall-runoff and is transported in the water phase. Bioavailable P originates from soil particle detachment during erosion and is transported in the solid phase. Thus, DP and BPP are predicted separately by kinetic and enrichment ratio approaches, respectively. The BAP concentration of runoff is calculated as the sum of predicted DP and BPP concentrations.

Dissolved P. Concentrations of DP in runoff are predicted by the following equation, which describes the kinetics of soil P desorption [33]:

$$P_r = \frac{K P_a D B t^\alpha W^\beta}{V} \quad [1]$$

where DP concentration of an individual runoff

event (mg L^{-1}), P_a is available soil P content (Bray I, mg kg^{-1}) of surface soil (0–50 mm) before each runoff event, D is effective depth of interaction between surface soil and runoff water (mm), B is bulk density of soil (Mg m^{-3}), t is duration of the runoff event (min), W is runoff water/soil (suspended sediment) ratio, V is total runoff during the event (mm), and K , α , and β are constants for a given soil. Values of K , α , and β were estimated from the ratio of surface soil clay/organic C content [28]. Values of D were estimated from soil loss (kg ha^{-1}):

$$\text{Ln}(D) = i(A) + 0.576 \text{Ln}(\text{soil loss}) \quad [2]$$

where i is a function of soil aggregation (A) [29]. In a simulated rainfall study, Sharpley [29] found that D was a function of rainfall intensity and soil slope and cover, the effects of which could be summarized by soil loss.

Bioavailable particulate P. The selective transport of clay-sized particles in runoff has led to the concept of enrichment ratios (ER) for P, which is defined as the ratio of the P content of eroded sediment to that of surface soil. The concentration of BPP in each runoff event is calculated from the BAP content of surface soil using a bioavailable soil P enrichment ratio (ER);

$$\text{Bioavailable Particulate P} = (\text{Soil Bioavailable P}) \cdot (\text{Sediment Concentration}) \cdot (\text{ER}) \quad [3]$$

where the units for bioavailable soil P are mg kg^{-1} and g L^{-1} for sediment concentration in runoff. The ER was predicted from soil loss (kg ha^{-1}) for each runoff event, using the following equation developed by Sharpley [30]:

$$\text{Ln}(ER) = 1.21 - 0.16 \text{Ln}(\text{soil loss}) \quad [4]$$

Predictions were compared to measured values using linear regression analysis, analysis of variance for paired data, and standard error of the y estimate. In the latter analysis, the measured value (x) was assumed to be correct and have no error, with the standard error in the predicted value (y) representing all variability associated with the predictive equations.

The concentration of DP and BPP of each runoff event was predicted using Eqs. [1]

through [4]; soil loss; surface soil clay content, aggregation, and organic C; and available (Bray I), bioavailable (Fe-oxide strip P), and TP content of surface soil before runoff. As equation constants calculated from soil physical and chemical properties [28], all equation parameters were independently determined with no field calibration conducted. Values of the constants and soil properties used in the prediction equations are given in Table 9.

Measured and predicted mean annual BAP concentrations were not different ($p < 0.05$) for all watersheds and management practices over a wide range in measured values (0.11 to 1.65 mg L⁻¹) (Fig. 4). However, BAP concentrations of runoff from grassed and no till watersheds were slightly underestimated (Fig. 4). The error in BAP prediction was 0.10 mg L⁻¹, which was 16% of the measured mean annual loss for all watersheds and management practices. When BAP losses were above 0.50 mg L⁻¹, measured and predicted values followed a 1:1 relationship (Fig. 4).

The underestimation of DP, BPP, and thus BAP concentration and loss in runoff from native grass and no till watersheds, may result from an inadequate representation of the contribution of P release from vegetative material and the enrichment of organic material to P transport in runoff. Vegetative cover affects both chemical and physical processes controlling P release from soil and crops to runoff water and soil loss in runoff. However, there has been limited success in simulating the effect of vegetative cover on P loss in runoff, particularly for growing plants [27].

Predicted values of ER are affected more by an incremental increase in soil loss at rates <50 kg ha⁻¹ yr⁻¹ than at rates >500 kg ha⁻¹

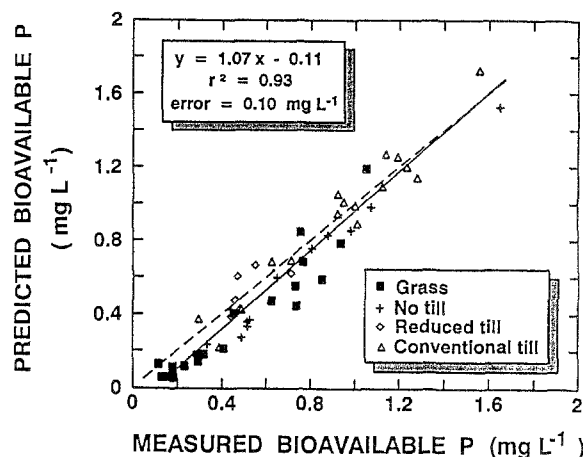


Fig. 4. Relationship between predicted and measured mean annual bioavailable P concentration of runoff.

yr⁻¹ because the relationship predicting ER from soil loss (Eq. [4]) is logarithmic. Consequently, making the slope and intercept of Eq. [3] a function of factors affecting soil loss or runoff, such as rainfall intensity, vegetative cover, and management practice, should improve predictions. This may involve use of specific surface area and density of eroded material and enrichment of particle size fractions, rather than total soil loss.

Conclusions

The amount of P removed from a 1 g sample of soil in 40 mL of 0.01 M CaCl₂ or 50 mL of unfiltered runoff by the Fe-oxide strip, during overnight shaking, can be used as a convenient and interference-free method to routinely estimate the BAP content of agricultural soils or runoff, respectively. As the strips act as a P-sink, they simulate P removal from soil or sediment-

Table 9. Values of equation parameters for the major soil types at each watershed location

Parameter	Cobb	Kirkland	Pullman	Woodward
Clay content, %	17	13	30	32
Organic C, g kg ⁻¹	3.2	20.2	8.3	10.2
Bulk density, Mg m ⁻³	1.35	1.40	1.45	1.40
Soil aggregation*	20	26	15	19
K	0.039	0.172	0.052	0.057
α	0.095	0.298	0.117	0.127
β	0.775	0.313	0.657	0.618
i	-1.71	-1.28	-2.07	-1.78

*Ratio of percent clay in dispersed/undispersed soil.

water samples by plant roots and algae. Thus, the Fe-oxide strip method has a stronger theoretical justification for its use over chemical extractants to estimate BAP.

The Fe-oxide strip method will aid BAP measurement in situations where laboratory facilities are minimal. For example, prepared Fe-oxide strips may be sent to a field location and BAP measured using only a 100 to 500 mL bottle in which a strip and soil or runoff sample is shaken overnight. The strip may then be dried and returned to an analytical laboratory for P removal and measurement. In the case of runoff, this would avoid potential problems with P transformations during sample storage and shipping. Further, strip P development with the use of prepackaged color reagents may allow P determination in the field by comparison with a standard color chart.

As the strip P content of soil was closely correlated with resin P and P tests for soils on which the test is recommended, it is possible that Fe-oxide strips may extract amounts of P related to plant availability for soils varying widely in properties. These relationships do not solely justify adoption of Fe-oxide strips as a new procedure to quantify P uptake. However, they emphasize the potential universality of the strip method to estimate plant-available soil P and suggest further evaluation is warranted.

Conventional soil test methods such as Bray I, Mehlich III, and Olsen, have been designed to assess the availability of soil P to optimize crop production. Thus, they may not measure forms of soil P most important to eutrophication. However, it has been shown that the Fe-oxide strips remove BAP from soil or runoff samples. Thus, the strip method may also be appropriate as an environmental soil test to assess the potential of a soil to enrich P in runoff.

Use of the proposed Fe-oxide strip method on runoff from agricultural watersheds in the Southern Plains over the last 3 yr, indicated that although BAP losses were reduced by practices minimizing runoff and erosion, even though the proportion of P transported in bioavailable forms can increase. Both TP (35 to 83%) and PP bioavailability (20 to 58%) varied appreciably with agricultural management. Thus, BAP is a dynamic function of physical, chemical, and

biological processes controlling both DP and BPP transport. Dissolved P transport is a function of desorption-dissolution reactions controlling P release from soil, fertilizer reaction products, vegetative cover, and decaying plant residues. On the other hand, BPP is a function of physical processes controlling erosion and particle-size enrichment and chemical properties of the eroded soil material governing P sorption and availability. Therefore, the continued measurement of BAP is recommended to evaluate reliably the impact of agricultural management on the biological productivity of surface waters.

The transport of BAP in soluble and particulate forms in runoff from various agricultural management practices, can be accurately predicted by the kinetic and enrichment ratio approaches used when BAP concentrations exceeded 0.50 mg L^{-1} . Above this value, BAP loss will have the greatest environmental impact. An additional advantage of these equations is that no field calibration was required. Overall, concentrations were predicted with 16% of measured values.

Although the loss of P in runoff from the study watersheds is not of general agronomic importance, concentrations exceeded limits recognized as stimulating accelerated eutrophication of surface waters (0.01 and 0.02 mg L^{-1} for DP and TP, respectively), even in runoff from unfertilized native grass watersheds. Thus, simulation of BAP, in addition to DP and TP transport, may improve the prediction of agricultural management effects on the biological response of receiving water bodies.

Several cautionary notes must be sounded, however, in relating BAP transport in runoff to the potential increase in algal growth in a lake. For example, in many lakes the surface photic zone may be shallow, due to sediment entrainment by wind or other current induced mixing. Further, suspended sediment comprised of silt-sized aggregates of clay ($>2 \mu\text{m}$), will settle more rapidly from the photic zone than smaller-sized primary particles. These factors can reduce the actual bioavailability of P input to lakes. Thus, strip P represents short-term BAP ($<30 \text{ d}$), that could be utilized by algae in the photic zone of lakes under aerobic conditions.

Once sediment settles to the bottom of a lake,

sediment P bioavailability may be increased by development of reducing conditions at the sediment-water interface. Under these conditions, strip P may underestimate P bioavailability and a stronger or more severe extractant, such as citrate-dithionite-bicarbonate, which removes a greater portion of Fe- and Al-bound P, should more accurately reflect long-term bioavailability (>30 d) of sediment P in the anoxic hypolimnion of stratified lakes. Consequently, BAP estimates should be used with information on the physiochemical properties of source sediment (e.g., degree of aggregation, texture, settling velocity, and clay mineralogy) and receiving lake (e.g., depth of photic zone, degree of surface mixing, development of reducing conditions, and water residence time).

Use of Fe-oxide strips may facilitate estimation of the potentially bioavailability of P transported in agricultural runoff and may thereby, improve assessment of the resultant impact on the biological productivity of receiving water bodies.

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